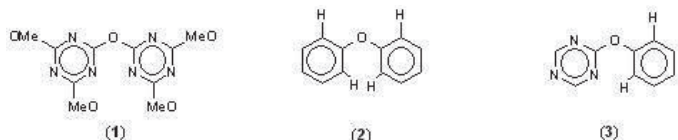


**P08.09.71***Acta Cryst.* (2008). A64, C440**Asymmetric reactivity of a symmetric di-s-triazinyl ether**Marek L Glowka<sup>1</sup>, Michal P Blaszczyk<sup>1</sup>, Andrzej Olczak<sup>1</sup>, Janina E Kaminska<sup>2</sup><sup>1</sup>Technical University of Lodz, Chemistry - 117, ul. Zeromskiego 116, Lodz, 90-924, Poland, <sup>2</sup>Technical University of Lodz, Institute of General Food Chemistry, ul. Wolczanska 171/173, 90-924 Lodz, Poland, E-mail : marekglo@p.lodz.pl

While studying acylation of less reactive nucleophiles by 2-acyloxy-4,6-dimethoxy-1,3,5-triazine, a crystalline byproduct **1** was isolated and its X-ray structure determined. The study showed significant molecular asymmetry of **1**. Comparison of its geometry with those of diaromatic ethers (CSD) revealed several regularities, concerning conjugation: - maximal conjugation of both rings requires their coplanarity, which is hindered by spatial repulsions; - in mixed ethers **3** the triazine shows always better conjugation; - in asymmetric diphenyl ethers **2** substituents influence conjugation; - in symmetric ethers **2** packing influence conjugation through AGIBA effect. The observed asymmetry of **1** enable us to use it as a gentle alkylation (by a triazine residue) agent.



Keywords: symmetric ethers, s-triazine ethers, AGIBA effect in aromatic ethers

**P08.09.72***Acta Cryst.* (2008). A64, C440**Mononuclear Rh(II) PNP-type complexes. Structure and reactivity**Yael M. Diskin-Posner, Moran Feller, Eyal Ben-Ari, Tarkeshwar Gupta, Linda J.W. Shimon, Gregory Leitus, Lev Weiner, David Milstein  
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While Rh(I) and Rh(III) complexes are ubiquitous, and have found many uses, Rh(II) complexes are less common. In particular, mononuclear Rh(II) complexes are relatively rare. Herein, we report on the synthesis of (PNPtBu)Rh(II) complexes (PNPtBu = 2,6-bis-(di-tert-butyl phosphino methyl)pyridine), their characterization and reactivity. The Rh(II) mononuclear complexes [(PNPtBu)RhCl][BF<sub>4</sub>] (**2**), [(PNPtBu)Rh(OC(O)CF<sub>3</sub>)] [OC(O)CF<sub>3</sub>] (**4**) and [(PNPtBu)Rh(acetone)][BF<sub>4</sub>]<sub>2</sub> (**6**) were synthesized by oxidation of the corresponding Rh(I) analogs with silver salts. On the other hand, treatment of (PNPtBu)RhCl with AgOC(O)CF<sub>3</sub> led only to chloride abstraction, with no oxidation. Complexes **2** and **6** were characterized by X-ray diffraction, EPR, cyclic voltammetry and dipole moment measurements. Although the paramagnetic complexes are relatively stable, they exhibit interesting reactivity. The mono- and di-cationic Rh(II) complexes [(PNPtBu)RhCl][BF<sub>4</sub>] (**2**) and [(PNPtBu)Rh(acetone)][BF<sub>4</sub>]<sub>2</sub> (**6**) exhibit different reactivity patterns. While complex **6** is reduced to Rh(I) in the presence of isonitriles or CO, complex **2** disproportionates in the presence of

acetonitrile, isonitriles or CO. Complexes **2** and **6** are reduced in the presence of phosphines and water to Rh(I) complexes. In case of complex **2** and triphenylphosphine, the reduced Rh(I) complex undergoes protonation to give a Rh(III) complex with a coordinated BF<sub>4</sub> [(PNPtBu)Rh(Cl)(H)(BF<sub>4</sub>)].

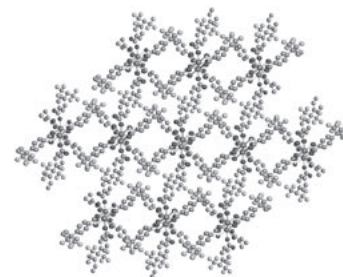
Keywords: rhodium compounds, catalysts, organometallic Complexes

**P08.09.73***Acta Cryst.* (2008). A64, C440**Design of new MOFs based on alkaline earth metals with promising catalytic applications**Ana E. Platero-Prats<sup>1</sup>, Victor A. De la Peña-O'Shea<sup>2</sup>, Felipe Gándara<sup>1</sup>, Natalia Snejko<sup>1</sup>, Ángeles Monge<sup>1</sup>, Enrique Gutiérrez-Puebla<sup>1</sup><sup>1</sup>Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), Sintesis y Estructura de Oxidos, Sor Juana Ines de la Cruz, 3, Cantoblanco, Madrid, Madrid, 28049, Spain, <sup>2</sup>Instituto Madrileño de Estudios Avanzados en Energia (IMDEA ENERGIA), Tulipán s/n, Móstoles, Madrid, 28933, Spain, E-mail : aplatero@icmm.csic.es

The design of new porous 3D polymeric structures is becoming increasingly important, due to their applications as catalysts and molecular sieves. Our group has great experience in the design of 3D metal-organic frameworks (MOFs) involving the use of long flexible linker ligands (eg. 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (H<sub>2</sub>hfpbb)). Thus, new unexpected structures have been synthesised with Zn, In and rare-earth elements [1-3]. This work deals with the design of new MOFs based on alkaline earth metals and H<sub>2</sub>hfpbb. The use of these elements has been less explored in this field, despite their interesting sorption (e. g. CO<sub>2</sub> fixation) and catalytic properties (e. g. Lewis acid catalysts). Thus, a new porous polymeric calcium structure with an unusual topology has been described. DFT calculates were performed in order to study the stability, as well as to understand the behaviour of the active site of these materials. Moreover, studies have been done to evaluate the catalytic and sorption properties of new MOFs based on Mg, Sr, Ba.

1. A. Monge *et al.*, *Chem. Commun.* **2005**, 1291
2. F. Gandara *et al.*, *Chem. Matter.*, **2008**, 20, 72
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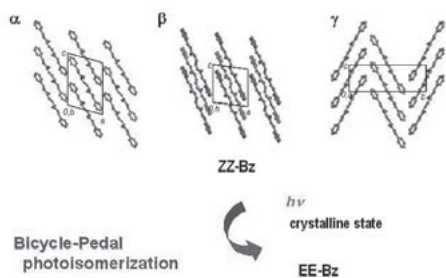
Keywords: organic inorganic hybrid materials, microporous materials, catalysis

**P08.09.74***Acta Cryst.* (2008). A64, C440-441**Change in the molecular structure of muconic esters during photoisomerization in the solid state**

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Organic reactions performed in the solid state have many intrinsic features for synthetic and materials chemistry because of the extremely high selectivity of the reactions. A limited number of the *E-Z* isomerizations of olefins in the crystalline state have been reported because of the difficulty in the inevitable change in the size and shape of the space occupied by the substituents of a double bond. Presently, we have revealed a change in the molecule structure of muconic esters, by the direct observation of single crystal structures during photoisomerization in the solid state. Benzyl (*Z,Z*)-muconate (*ZZ-Bz*) afford three polymorphs. During the solid-state photoisomerization of these polymorphs to the corresponding (*E,E*)-muconate (*EE-Bz*), it was revealed that the isomerization occurs via a topochemical reaction process according to a bicycle-pedal model and is finally accompanied by a phase transition to a stable crystal structure. After photoirradiation of powdered *ZZ-Bz*, the conversion to *EE-Bz* depended on the structure of the polymorphs. A difference in the reactivity is discussed on the basis of the molecular structures and the void space in polymorphic crystals.



Keywords: cis-trans isomerization, polymorphs, single crystals

### P08.09.75

*Acta Cryst.* (2008). A64, C441

#### Defects in single crystalline Ge-doped silicon revealed by annealing under high hydrostatic pressure

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Germanium - doped Czochralski grown silicon (Cz-Si:Ge) with cGe exceeding 1 at.% has been rediscovered because Ge introduces controlled strain into layered structures, with carrier mobility competitive to the case of III-V semiconductors. Annealing of Cz-Si:Ge with low Ge content under enhanced hydrostatic pressure (HP) at high temperature (HT) results in specific structural transformations, of interest for integrated circuits technology. Defects in Cz-Si:Ge, with cGe = 1.4x10<sup>-3</sup> and 1.4-7.6 at.%, containing also oxygen in a concentration up to 1x10<sup>18</sup> cm<sup>-3</sup>, and processed at up to 1400 K under HP up to 1.2 GPa were investigated by synchrotron topography, high resolution X-ray diffractometry, Infrared Spectroscopy, photoluminescence (PL) and related methods. Topography of Cz-Si:Ge reveals uniform structure in the case of cGe = 1.4x10<sup>-3</sup> at.% while Ge segregation is detected for Cz-Si:Ge with cGe exceeding 1.4 at.%. The presence of dislocations at 10(3) cm<sup>-2</sup> density has been stated after processing. X-Ray diffuse scattering is most pronounced for the samples with cGe = 2.6 at.%; its intensity decreases with HT (HP). Annealing at 1270 K for 5 h resulted in the increased lattice parameter (a), e.g. for Cz-Si:Ge with cGe =1.4

at.%, a=0.5440574 nm, 0.5441908 nm if annealed under 10(5) Pa but 0.5441113 nm after processing under 1.1 GPa. The PL intensity at 1.07 eV, related to the presence of electron-hole droplets, decreased after processing, evidencing out-annealing of point-like defects under HP. The effect of HT - HP on Cz-Si:Ge is related, among others factors, to stress-induced activation of Ge clusters promoting precipitation of interstitial oxygen. On the other hand, the treatment under HP results in the improved overall homogeneity of Cz-Si:Ge.

Keywords: microstructure, Si-Ge, annealing

### P08.09.76

*Acta Cryst.* (2008). A64, C441

#### Structure of synthesized nano-sized perovskite oxide La<sub>1-x</sub>Ce<sub>x</sub>CoO<sub>3</sub>

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Nanosized La<sub>1-x</sub>Ce<sub>x</sub>CoO<sub>3</sub> (x<0.1) cobaltide oxide powder with perovskite structure was synthesized at different calcination temperatures using the amorphous heteronuclear complex La<sub>1-x</sub>Ce<sub>x</sub>Co(DTPA)6H<sub>2</sub>O (x=0.1) as precursor. The effects of the calcination temperature was examined by XRD, TEM and BET methods. The crystal structure of perovskite type La<sub>1-x</sub>Ce<sub>x</sub>CoO<sub>3</sub> (x<0.1) was refined by X-ray Rietveld analysis for three different calcination temperatures, and its correlation with catalytic activities is discussed. The results indicated that the La<sub>1-x</sub>Ce<sub>x</sub>CoO<sub>3</sub> (x<0.1) cobaltide oxide powder is not of pure perovskite type and with increasing calcination temperature from T = 600 °C to T = 900 °C the grain size of La<sub>1-x</sub>Ce<sub>x</sub>CoO<sub>3</sub> (x<0.1) increases. The specific surface area varies from 4.347 to 9.016 m<sup>2</sup>/g. The results reveal that the calcination temperature plays a key role in controlling the morphology, crystallization and phase compositions of La<sub>1-x</sub>Ce<sub>x</sub>CoO<sub>3</sub> (x<0.1) perovskite type oxide. After being calcined at T = 800 °C for 3 h, the La<sub>1-x</sub>Ce<sub>x</sub>CoO<sub>3</sub> (x<0.1) catalyst exhibits the highest catalytic activity for carbon monoxide oxidation.

Keywords: perovskite oxide, X-ray powder diffraction, catalytic combustion

### P08.09.77

*Acta Cryst.* (2008). A64, C441-442

#### New insights into the Mo-Sn bond in binuclear complexes

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